SYNTHESIS OF ALKOXY DERIVATIVES OF DECAHYDRO-*closo*-DECABORATE ANION+

Alexander V. PRIKAZNOV[a1,b], Vikentii I. BRAGIN[a2,*], Margarita N. DAVYDOVA[b], Igor B. SIVAEV[a3] and Vladimir I. BREGADZE[a4]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 119991 Moscow, Russia; e-mail:* [1] *s-ineos@mail.ru,* [2] *bragin@nmrcenter.ru,* [3] *sivaev@ineos.ac.ru,* [4] *bre@ineos.ac.ru*

[b] *M. V. Lomonosov Moscow Academy for Fine Chemical Technology, Vernadskii Pr. 86, 117571 Moscow, Russia*

Received August 31, 2007
Accepted November 12, 2007

Synthesis of alkoxy derivatives of *closo*-decaborate anion [1- and 2-$B_{10}H_9OR]^{2-}$ by reaction of the hydroxy derivatives with corresponding alkyl bromides was described. A new method of synthesis of 2-hydroxy derivative of *closo*-decaborate anion [2-$B_{10}H_9OH]^{2-}$ was proposed.
Keywords: Boranes; Boron clusters; *closo*-Decaborate; Hydroxyboranes; Alkoxyboranes.

The decahydro-*closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ (Fig. 1) has been considered as potential boron moiety for boron neutron capture therapy of cancer[2].

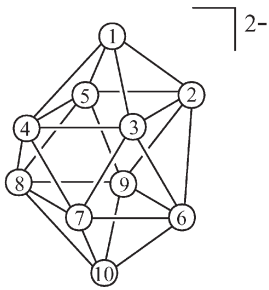


FIG. 1
Structure and numbering of atoms in the $[B_{10}H_{10}]^{2-}$ anion

+ Preliminary results of this study, see ref.[1]

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 12, pp. 1689–1696

doi:10.1135/cccc20071689

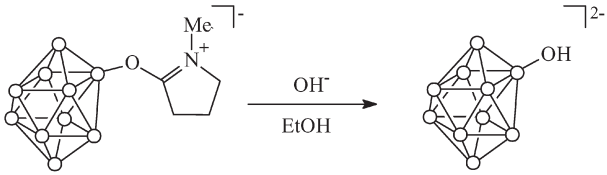
A common approach has been to use the decaborate clusters either alone[3] or attached to high-capacity carriers such as poly(amidoamine) (PAMAM or "starburst") dendrimers (macromolecules that can be linked to receptor-specific targeting agents)[4]. The use of *closo*-decaborate-substituted four- or five-generation PAMAM dendrimers as high-capacity carriers conjugated to monoclonal antibodies[5,6], bispecific antibodies[7], and epidermal growth factor[8–10] to target brain tumors, or folic acid[11] and vascular endothelial growth factor[12] to target other tumor types have been described. More recently the *closo*-decaborate was shown to be reasonable linker for attachment of radiohalogens to tumor-targeting proteins and peptides in radionuclide diagnostics and therapy[13]. Development of medicin applications of the *closo*-decaborate anion stimulates synthesis of novel functional compounds on its basis. Recently we reported synthesis of Schiff bases and benzylamines as well as its hydroxy derivative[16] derived from the *closo*-decaborate anion[14,15]. In this contribution we report synthesis of 1- and 2-alkoxy derivatives of the *closo*-decaborate anion by alkylation of the corresponding hydroxy derivatives.

RESULTS AND DISCUSSION

Synthesis of both isomers of hydroxy derivatives of the *closo*-decaborate anion, $[1\text{-}B_{10}H_9OH]^{2-}$ and $[2\text{-}B_{10}H_9OH]^{2-}$, was described recently. The 1-hydroxy-*closo*-decaborate was prepared by the reaction of the corresponding diazonium derivative $[1\text{-}B_{10}H_9N_2]^-$ with hydroxide ions[15] and the 2-hydroxy-*closo*-decaborate was obtained by alkaline hydrolysis of the corresponding acetate $[2\text{-}B_{10}H_9OC(O)Me]^{2-}$ (ref.[17]). However, in our hands the latter method did not give the pure product. This could be explained by formation of admixture of di- and/or triacetates in the synthesis of $[2\text{-}B_{10}H_9OC(O)Me]^{2-}$ (ref.[18]), which hydrolysis, results in admixture of corresponding hydroxy derivatives. Similar situation takes place in the synthesis of hydroxy derivative of the *closo*-dodecaborate anion $[B_{12}H_{11}OH]^{2-}$ by alkaline hydrolysis of the corresponding acetate $[B_{12}H_{11}OC(O)Me]^{2-}$; however, in this case admixture of dihydroxy derivatives can be easily removed due to different solubility of tetrabutylammonium salts of the mono- and dihydroxy derivatives in water[19].

To prepare pure $[2\text{-}B_{10}H_9OH]^{2-}$ we developed a new method based on alkaline hydrolysis of *N*-methylpyrrolidonium derivative of the *closo*-decaborate anion $[2\text{-}B_{10}H_9NMP]^-$ (Scheme 1). This method have advantage of easy purification of anionic $[2\text{-}B_{10}H_9NMP]^-$ from admixture of neutral disubstituted derivatives $[B_{10}H_8(NMP)_2]$. A previous similar approach was

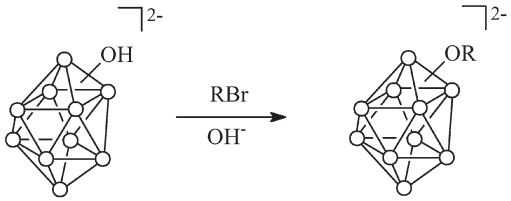
proposed for synthesis of the hydroxy derivative of the *closo*-dodecaborate anion $[B_{12}H_{11}OH]^{2-}$ (refs[20,21]). Synthesis and X-ray structure of $[2\text{-}B_{10}H_9NMP]^-$ were described earlier[20,22]. We found that the tetrabutylammonium salt of the *N*-methylpyrrolidonium derivative can be used as convenient precursor for preparation of the 2-hydroxy derivative. Alkaline hydrolysis of $(Bu_4N)[2\text{-}B_{10}H_9NMP]$ in refluxing 1 M ethanolic KOH overnight resulted in formation of insoluble in ethanol potassium salt $K[2\text{-}B_{10}H_9OH]$ insoluble in ethanol completely free of admixtures of dihydroxy derivatives and the *closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ (always present in small amounts in the starting *closo*-decaborate). The potassium salt has good water solubility and can easily be transformed into other salts by precipitation from water or using ion-exchangers.



SCHEME 1

To make the alkylation procedure uniform for both isomers of hydroxy derivative the potassium salt $K_2[2\text{-}B_{10}H_9OH]$ was converted to the corresponding benzyltriphenylphosphonium salt by treatment with $(Ph_3PCH_2Ph)Cl$ in aqueous solution.

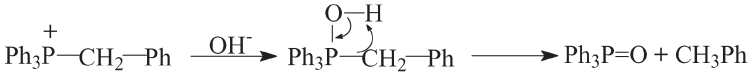
Alkylation of the hydroxy derivative of the *closo*-dodecaborate anion $[B_{12}H_{11}OH]^{2-}$ was described previously[23,24]. In this study we carried out alkylation of both isomers of hydroxy derivative of *closo*-decaborate anion under conditions described earlier for alkylation of the hydroxy-*closo*-dodecaborate anion (DMSO, KOH; room temperature)[23]. Ethyl bromide, propyl bromide, butyl bromide and isopentyl bromide were used as alkylating agents (Scheme 2).



R=C_2H_5, $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH(CH_3)_2$

SCHEME 2

The benzyltriphenylphosphonium cation was degraded by excess of potassium hydroxide giving triphenylphosphine oxide[25] (Scheme 3).



SCHEME 3

As a result, the alkoxy derivatives were obtained as water-soluble potassium salts and isolated as the tetraphenylphosphonium salts by precipitation with $[Ph_4P]Cl$ from aqueous solution. The cation of choice allows to avoid overlap of the cation and anion signals in ^1H NMR spectra.

All the compounds prepared were characterized by the ^1H, ^{13}C, and ^{11}B NMR spectroscopy. Analysis of the ^1H NMR spectra of alkoxy *closo*-decaborates revealed that the signals of the O-bonded methylene groups of the 1-alkoxy derivatives $[1\text{-}B_{10}H_9OR]^{2-}$ (3.80–3.86 ppm) appear of lover fields than the corresponding signals of the 2-alkoxy derivatives $[2\text{-}B_{10}H_9OR]^{2-}$ (2.90–3.01 ppm). This difference can be ascribed to a stronger electron-donor effect of the *closo*-2-decaborate group than the *closo*-1-decaborate group.

CONCLUSIONS

A series of alkoxy derivatives of *closo*-decaborate anion $[1\text{-}B_{10}H_9OR]^{2-}$ and $[2\text{-}B_{10}H_9OR]^{2-}$ (R = C_2H_5, C_3H_7, C_4H_9, *i*-C_5H_{11}) was prepared by alkylation of the corresponding hydroxy derivatives. The compounds prepared were characterized by the ^1H, ^{13}C, and ^{11}B NMR spectroscopy. A new method of synthesis of 2-hydroxy derivative of *closo*-decaborate anion $[2\text{-}B_{10}H_9OH]^{2-}$ was proposed.

EXPERIMENTAL

$(Ph_3PCH_2Ph)_2[1\text{-}B_{10}H_9OH]$ was prepared as described in[16]. The ^1H, ^{13}C and ^{11}B NMR spectra (δ, ppm; *J*, Hz) were collected using Bruker AM360 and Bruker Avance-400 spectrometers. Signals in the ^{11}B NMR spectra of $(Bu_4N)[2\text{-}B_{10}H_9NMP]$, $(Ph_4P)_2[1\text{-}B_{10}H_9OEt]$ and $(Ph_4P)_2$-$[2\text{-}B_{10}H_9OEt]$ were assigned using ^{11}B-^{11}B COSY NMR spectroscopy, an assignment of signals in other ^{11}B NMR spectra was given on analogy with spectra of the corresponding ethoxy derivatives.

Synthesis of $(Bu_4N)[2\text{-}B_{10}H_9NMP]$

To $(Et_3NH)_2[B_{10}H_{10}]$ (3.00 g, 9.2 mmol) and *N*-methylpyrrolidone (50 ml) trifluoroacetic acid (2 ml) was added and the reaction mixture was stirred with heating at 60–80 °C until hydro-

gen evolution ceased (ca. 24 h). The reaction mixture was cooled to room temperature and the excess of *N*-methylpyrrolidone was distilled off under reduced pressure (12 mm Hg). The residue was dissolved in water (100 ml) and treated with $(Bu_4N)Br$ (3.00 g, 9.3 mmol) in water (20 ml). The precipitate formed was filtered off, washed with water and dried over P_2O_5 to give 2.30 g (53%) of the white product. ^{1}H NMR (400 MHz, DMSO-d_6): 3.62 t, 2 H (N-C**H**$_2$-); 3.34 s, 3 H (N-C**H**$_3$); 3.16 t, 8 H (Bu_4N^+); 3.11 t, 2 H (=C-C**H**$_2$-); 2.07 m, 2 H (-CH$_2$C**H**$_2$CH$_2$-); 1.57 m, 8 H (Bu_4N^+); 1.32 m, 8 H (Bu_4N^+); 0.93 t, 12 H (Bu_4N^+). ^{13}C NMR (90 MHz, DMSO-d_6): 178.0 (C=N); 58.0 (Bu_4N^+); 51.1 (N-C**H**$_2$-); 31.2 (N-C**H**$_3$); 29.5 (=C-C**H**$_2$-); 23.5 (Bu_4N^+); 19.6 (Bu_4N^+); 17.3 (-CH$_2$C**H**$_2$CH$_2$-); 13.9 (Bu_4N^+). ^{11}B NMR (115 MHz, CD_3OD): –0.8 s, 1 B (B(2)); –2.6 d, 1 B, J = 134 (B(10)); –5.9 d, 1 B, J = 135 (B(1)); –24.1 d, 2 B, J = 119 (B(7,8)); –25.1 d, 2 B, J = 118 (B(3,5)); –30.3 d, 2 B, J = 126 (B(6,9)); –32.8 d, 1 B, J = 128 (B(4)). IR (Nujol, cm^{-1}): 2492 (ν_{BH}), 2469 (ν_{BH}), 2432 (ν_{BH}), 1662 ($\nu_{C=N}$).

Synthesis of $K_2[2\text{-}B_{10}H_9OH]$

$(Bu_4N)[2\text{-}B_{10}H_9NMP]$ (2.00 g, 4.02 mmol) was dissolved in 1 M solution of KOH in ethanol (80 ml) and heated at 60 °C overnight. The precipitate formed was filtered off, washed with cold ethanol and dried in air to give 0.70 g (81%) of $K_2[2\text{-}B_{10}H_9OH]$. ^{11}B NMR (128 MHz, D_2O): –2.9 s+d, 2 B, J = 139; –4.8 d, 1 B, J = 139; –22.9 d, 4 B, J = 119; –28.3 d, 2 B, J = 110; –34.6 d, 1 B, J = 120. IR (Nujol, cm^{-1}): 3646 (ν_{OH}), 2499 (ν_{BH}), 2452 (ν_{BH}), 2423 (ν_{BH}).

Synthesis of $(Ph_3PCH_2Ph)_2[2\text{-}B_{10}H_9OH]$

A solution of $K_2[2\text{-}B_{10}H_9OH]$ (0.56 g, 2.60 mmol) in water (20 ml) was treated with $[Ph_3PCH_2Ph]Cl$ (2.10 g, 5.40 mmol) in water (25 ml). The precipitate formed was filtered off, washed with water and dried over P_2O_5 to give 1.58 g (72%) of $(Ph_3PCH_2Ph)_2[2\text{-}B_{10}H_9OH]$. ^{11}B NMR spectrum (128 MHz, DMSO-d_6): –3.2 s+d, 2 B, J = 145; –4.5 d, 1 B, J = 140; –22.8 d, 4 B, J = 121; –28.1 d, 2 B, J = 119; –34 d, 1 B, J = 125.

Synthesis of Alkoxy Derivatives $(Ph_4P)_2[1\text{-}B_{10}H_9OR]$ and $(Ph_4P)_2[2\text{-}B_{10}H_9OR]$. General Procedure

To a solution of $(Ph_3PCH_2Ph)_2[1\text{-}B_{10}H_9OH]$ or $(Ph_3PCH_2Ph)_2[2\text{-}B_{10}H_9OH]$ (0.40 g, 0.48 mmol) in DMSO (20 ml), KOH (0.14 g, 2.42 mmol) and alkyl bromide (4.80 mmol) were added and the reaction mixture was stirred at room temperature for 2 days. DMSO was distilled off under reduced pressure (12 mm Hg), and the residue was dissolved in ethanol followed by addition of water. The solution obtained was concentrated in vacuo, the precipitated triphenylphosphine oxide was filtered off and the filtrate was treated with a solution of $[Ph_4P]Cl$ (0.36 g, 0.96 mmol) in water. The precipitate formed was filtered off, washed with water, and dried over P_2O_5.

$(Ph_4P)_2[1\text{-}B_{10}H_9OEt]$. Yield 0.28 g (70%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.90 m, 8 H (Ph_4P^+); 7.70 m, 32 H (Ph_4P^+); 3.80 q, 2 H, J = 7.6 (-OC**H**$_2$CH$_3$); 1.15 t, 3 H, J = 7.7 (-OCH$_2$C**H**$_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.8 (Ph_4P^+); 135.0 (Ph_4P^+); 134.9 (Ph_4P^+); 131.0 (Ph_4P^+); 130.9 (Ph_4P^+); 118.4 (Ph_4P^+); 117.8 (Ph_4P^+); 66.2 (-OCH$_2$CH$_3$); 19.0 (-OCH$_2$C**H**$_3$). ^{11}B NMR (128 MHz, DMSO-d_6): 23.1 s, 1 B (B(1)); –13.8 d, 1 B, J = 134 (B(10)); –31.5 d, 4 B, J = 125 (B(2-5)); –33.5 d, 4 B, J = 126 (B(6-9).

$(Ph_4P)_2[2\text{-}B_{10}H_9OEt]$. Yield 0.20 g (50%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.90 m, 8 H (Ph_4P^+); 7.72 m, 32 H (Ph_4P^+); 3.01 q, 2 H, J = 7.6 (-OC**H**$_2$CH$_3$); 0.76 t, 3 H, J = 7.6

(-$OCH_2C\mathbf{H}_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 140.6 (Ph_4P^+); 139.8 (Ph_4P^+); 139.7 (Ph_4P^+); 135.8 (Ph_4P^+); 135.6 (Ph_4P^+); 123.4 (Ph_4P^+); 122.4 (Ph_4P^+); 70.4 (-$O\mathbf{C}H_2CH_3$); 23.5 (-$OCH_2\mathbf{C}H_3$). ^{11}B NMR (128 MHz, DMSO-d_6): –2.0 s, 1 B (B(2)); –3.2 d, 1 B, *J* = 139 (B(10)); –5.6 d, 1 B, *J* = 139 (B(1)); –23.8 d, 4 B, *J* = 109 (B(3,5,7,8)); –29.3 d, 2 B, *J* = 125 (B(6,9); –34.3 d, 1 B, *J* = 125 (B(4)).

$(Ph_4P)_2$[1-$B_{10}H_9OPr$]. Yield 0.21 g (50%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.83 m, 8 H (Ph_4P^+); 7.62 m, 32 H (Ph_4P^+); 3.80 t, 2 H, *J* = 6.5 (-$O\mathbf{C}H_2CH_2CH_3$); 1.66 m, 2 H (-$OCH_2C\mathbf{H}_2CH_3$); 0.90 t, 3 H, *J* = 7.2 (-$OCH_2CH_2C\mathbf{H}_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.0 (Ph_4P^+); 134.8 (Ph_4P^+); 134.5 (Ph_4P^+); 130.8 (Ph_4P^+); 130.3 (Ph_4P^+); 117.9 (Ph_4P^+); 117.4 (Ph_4P^+); 72.9 (-$O\mathbf{C}H_2CH_2CH_3$); 25.3 (-$OCH_2\mathbf{C}H_2CH_3$); 10.9 (-$OCH_2CH_2\mathbf{C}H_3$). ^{11}B NMR (128 MHz, DMSO-d_6): 23.3 s, 1 B (B(1)); –13.9 d, 1 B, *J* = 140 (B(10)); –32.2 d, 4 B, *J* = 131 (B(2-5)); –32.6 d, 4 B, *J* = 132 (B(6-9).

$(Ph_4P)_2$[2-$B_{10}H_9OPr$]. Yield 0.24 g (58%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.89 m, 8 H (Ph_4P^+); 7.68 m, 32 H (Ph_4P^+); 2.90 t, 2 H, *J* = 7.6 (-$O\mathbf{C}H_2CH_2CH_3$); 1.15 m, 2 H (-$OCH_2C\mathbf{H}_2CH_3$); 0.62 t, 3 H, *J* = 7.8 (-$OCH_2CH_2C\mathbf{H}_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.8 (Ph_4P^+); 135.0 (Ph_4P^+); 134.9 (Ph_4P^+); 131.0 (Ph_4P^+); 130.9 (Ph_4P^+); 118.4 (Ph_4P^+); 117.8 (Ph_4P^+); 72.9 (-$O\mathbf{C}H_2CH_2CH_3$); 25.6 (-$OCH_2\mathbf{C}H_2CH_3$); 11.2 ($OCH_2CH_2\mathbf{C}H_3$). ^{11}B NMR (128 MHz, DMSO-d_6): –2.0 s, 1 B (B(2)); –3.4 d, 1 B, *J* = 139 (B(10)); –5.5 d, 1 B, *J* = 137 (B(1)); –23.9 d, 4 B, *J* = 118 (B(3,5,7,8)); –29.3 d, 2 B, *J* = 110 (B(6,9)); –34.4 d, 1 B, *J* = 123 (B(4)).

$(Ph_4P)_2$[1-$B_{10}H_9OBu$]. Yield 0.33 g (78%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.78 m, 8 H (Ph_4P^+); 7.65 m, 32 H (Ph_4P^+); 3.83 t, 2 H, *J* = 6.9 (-$O\mathbf{C}H_2CH_2CH_2CH_3$); 1.63 m, 2 H (-$OCH_2C\mathbf{H}_2CH_2CH_3$); 1.38 m, 2 H (-$OCH_2CH_2C\mathbf{H}_2CH_3$); 0.92 t, 3 H, *J* = 7.3 (-$OCH_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.6 (Ph_4P^+); 135.1 (Ph_4P^+); 133.2 (Ph_4P^+); 131.0 (Ph_4P^+); 130.8 (Ph_4P^+); 118.4 (Ph_4P^+); 117.9 (Ph_4P^+); 71.3 (-$O\mathbf{C}H_2CH_2CH_2CH_3$); 35.2 (-$OCH_2\mathbf{C}H_2CH_2CH_3$); 19.8 (-$OCH_2CH_2\mathbf{C}H_2CH_3$); 14.8 (-$OCH_2CH_2CH_2\mathbf{C}H_3$). ^{11}B NMR (128 MHz, DMSO-d_6): 24.8 s, 1 B (B(1)); –14.8 d, 1 B, *J* = 140 (B(10)); –32.5 d, 4 B, *J* = 157 (B(2-5)); –33.8 d, 4 B, *J* = 144 (B(6-9)).

$(Ph_4P)_2$[2-$B_{10}H_9OBu$]. Yield 0.30 g (72%). ^{1}H NMR (360 MHz, DMSO-d_6): 7.9 m, 8 H (Ph_4P^+); 7.7 m, 32 H (Ph_4P^+); 2.92 t, 2 H, *J* = 7.1 (-$O\mathbf{C}H_2CH_2CH_2CH_3$); 1.12 m, 4 H (-$OCH_2C\mathbf{H}_2C\mathbf{H}_2CH_3$); 0.76 t, 3 H, *J* = 7.5 (-$OCH_2CH_2CH_2C\mathbf{H}_3$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.4 (Ph_4P^+); 134.8 (Ph_4P^+); 132.9 (Ph_4P^+); 130.5 (Ph_4P^+); 130.3 (Ph_4P^+); 117.9 (Ph_4P^+); 117.4 (Ph_4P^+); 70.2 (-$O\mathbf{C}H_2CH_2CH_2CH_3$); 34.5 (-$OCH_2\mathbf{C}H_2CH_2CH_3$); 18.9 (-$OCH_2CH_2\mathbf{C}H_2CH_3$); 14.2 (-$OCH_2CH_2CH_2\mathbf{C}H_3$). ^{11}B NMR (400 MHz, DMSO-d_6): –1.8 s, 1 B (B(2)); –3.3 d, 1 B, *J* = 135 (B(10)); –5.5 d, 1 B, *J* = 135 (B(1)); –23.8 d, 4 B, *J* = 111 (B(3,5,7,8); –29.2 d, 2 B, *J* = 124 (B(6,9)); –34.3 d, 1 B, *J* = 125 (B(4)).

$(Ph_4P)_2$[1-$B_{10}H_9OCH_2CH_2CHMe_2$]. Yield 0.38 g (81%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.89 m, 8 H (Ph_4P^+); 7.73 m, 32 H (Ph_4P^+); 3.86 t, 2 H, *J* = 6.9 (-$O\mathbf{C}H_2CH_2CH(CH_3)_2$); 1.77 m, 1 H (-$OCH_2CH_2C\mathbf{H}(CH_3)_2$); 1.54 m, 2 H (-$OCH_2C\mathbf{H}_2CH(CH_3)_2$); 0.91 d, 6 H, *J* = 6.6 (-$OCH_2CH_2CH(C\mathbf{H}_3)_2$). ^{13}C NMR (90 MHz, DMSO-d_6): 135.4 (Ph_4P^+); 134.8 (Ph_4P^+); 132.9 (Ph_4P^+); 130.5 (Ph_4P^+); 130.3 (Ph_4P^+); 117.9 (Ph_4P^+); 117.4 (Ph_4P^+); 69.4 (-$O\mathbf{C}H_2CH_2CH(CH_3)_2$); 41.6 (-$OCH_2\mathbf{C}H_2CH(CH_3)_2$); 24.9 (-$OCH_2CH_2\mathbf{C}H(CH_3)_2$); 23.0 (-$OCH_2CH_2CH(\mathbf{C}H_3)_2$). ^{11}B NMR (128 MHz, DMSO-d_6): 24.9 s, 1 B (B(1)); –14.9 d, 1 B, *J* = 139 (B(10)); –32.5 d, 4 B, *J* = 155 (B(2-5)); –33.8 d, 4 B, *J* = 144 (B(6-9)).

$(Ph_4P)_2$[2-$B_{10}H_9OCH_2CH_2CHMe_2$]. Yield 0.35 g (75%). ^{1}H NMR (400 MHz, DMSO-d_6): 7.91 m, 8 H (Ph_4P^+); 7.72 m, 32 H (Ph_4P^+); 2.96 t, 2 H, *J* = 7.5 (-$O\mathbf{C}H_2CH_2CH(CH_3)_2$); 1.42 m, 1 H (-$OCH_2CH_2C\mathbf{H}(CH_3)_2$); 1.04 m, 2 H (-$OCH_2C\mathbf{H}_2CH(CH_3)_2$); 0.73 d, 6 H, *J* = 6.9

(-$OCH_2CH_2CH(CH_3)_2$). ^{11}B NMR (128 MHz, DMSO-d_6): –1.8 s, 1 B (B(2)); –3.3 d, 1 B, J = 135 (B(10)); –5.4 d, 1 B, J = 135 (B(1)); –23.8 d, 4 B, J = 115 (B(3,5,7,8)); –29.3 d, 2 B, J = 110 (B(6,9)); –34.3 d, 1 B, J = 125 (B(4)).

This work was supported by the Russian Foundation for Basic Research (05-03-32429).

REFERENCES

1. Prikaznov A. V., Bragin V. I., Sivaev I. B., Davydova M. N., Bregadze V. I.: Presented at *IX Russian Youth Conference on Organic Chemistry, Moscow, December 15, 2006*.
2. Hawthorne M. F.: *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950.
3. Heber E., Trivillin V. A., Nigg D., Kreimann E. L., Itoiz M. E., Rebagliati R. J., Batistoni D., Schwint A. S.: *Arch. Oral Biol.* **2004**, *49*, 313.
4. Wu G., Barth R. F., Yang W., Lee R. J., Tjarks W., Backer M. V., Backer J. M.: *Anti-Cancer Agents Med. Chem.* **2006**, *6*, 167.
5. Barth R. F., Adams D. M., Soloway A. H., Alam F., Darby M. V.: *Bioconjugate Chem.* **1994**, *5*, 58.
6. Wu G., Barth R. F., Yang W., Chatterjee M., Tjarks W., Ciesielski M. J., Fenstermaker R. A.: *Bioconjugate Chem.* **2004**, *15*, 185.
7. Liu L., Barth R. F., Adams D. M., Soloway A. H., Reisfeld R. A.: *Anticancer Res.* **1996**, *16*, 2581.
8. Capala J., Barth R. F., Bendayan M., Lauzon M., Adams D. M., Soloway A. H., Fenstermaker R. A., Carlsson J.: *Bioconjugate Chem.* **1996**, *7*, 7.
9. Yang W., Barth R. F., Adams D. M., Soloway A. H.: *Cancer Res.* **1997**, *57*, 4333.
10. Yang W., Barth R. F., Wu G., Bandyopadhyaya A. K., Thirumamagal B. T., Tjarks W., Binns P. J., Riley K., Patel H., Coderre J. A., Ciesielski M. J., Fenstermaker R. A.: *Appl. Radiat. Isot.* **2004**, *61*, 981.
11. Shukla S., Wu G., Chatterjee M., Yang W., Sekido M., Diop L. A., Muller R., Sudimack J. J., Lee R. J., Barth R. F., Tjarks W.: *Bioconjugate Chem.* **2003**, *14*, 158.
12. Backer M. V., Gayunutdinov T. I., Patel V., Bandyopadhyaya A. K., Thirumamagal B. T., Tjarks W., Barth R. F., Claffey K., Backer J. M.: *Mol. Cancer Ther.* **2005**, *4*, 1423.
13. Wilbur D. S., Chyan M.-K., Hamlin D. K., Vessella R. L., Wedge T. J., Hawthorne M. F.: *Bioconjugate Chem.* **2007**, *18*, 1226.
14. Sivaev I. B., Votinova N. A., Bragin V. I., Starikova Z. A., Goeva L. V., Bregadze V. I., Sjöberg S.: *J. Organomet. Chem.* **2002**, *657*, 163.
15. Sivaev I. B., Bragin V. I., Bregadze V. I., Votinova N. A., Sjöberg S.: *Russ. Chem. Bull.* **2004**, *53*, 2092.
16. Bragin V. I., Sivaev I. B., Bregadze V. I., Votinova N. A.: *J. Organomet. Chem.* **2005**, *690*, 2847.
17. Zhizhin K. Yu., Malinina E. A., Polyakova I. N., Lisovskii M. V., Kuznetsov N. T.: *Russ. J. Inorg. Chem.* **2002**, *47*, 1158.
18. Zhizhin K. Yu., Vovk O. O., Malinina E. A., Mustyatsa V. N., Goeva L. V., Polyakova I. N., Kuznetsov N. T.: *Russ. J. Coord. Chem.* **2001**, *27*, 613.
19. Krause U., Preetz W.: *Z. Anorg. Allg. Chem.* **1995**, *621*, 516.
20. Knoth W. H., Sauer J. C., England D. C., Hertler W. R., Muetterties E. L.: *J. Am. Chem. Soc.* **1964**, *86*, 3973.

21. Semioshkin A. A., Petrovski P. V., Sivaev I. B., Balandina E. G., Bregadze V. I.: *Russ. Chem. Bull.* **1996**, *45*, 683.
22. Zhizhin K. Yu., Mustyatsa V. N., Malinina E. N., Polyakova I. N., Kuznetsov N. T.: *Russ. J. Inorg. Chem.* **2005**, *50*, 29.
23. Peymann T., Lork E., Gabel D.: *Inorg. Chem.* **1996**, *35*, 1355.
24. Sivaev I. B., Sjöberg S., Bregadze V. I., Gabel D.: *Tetrahedron Lett.* **1999**, *40*, 3451.
25. Xie W., Xie R., Pan W.-P., Hunter D., Koene B., Tan L.-S., Vafa R.: *Chem. Mater.* **2002**, 4837.